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A critical review on cellulose: From fundamental to an approach on sensor technology

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ABSTRACT

The interest in cellulose and its modification as cellulose-based composite has been exponentially increasing. During the last three decades, cellulose and cellulose-based composite have been extensively designed for many aspects of the sensor. Due to the sustainability of cellulose and its excellent properties, the use of cellulose and the modification on cellulose-based composite can be versatile in the sensor community. In this review article, fundamental and background of cellulose and modification of cellulose-based composite are presented. Numerous approaches on cellulose and cellulose-based composite for many types of sensors including gas sensor, humidity sensor, UV sensor, strain sensor as well as capacitive sensor were discussed.

Contents

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1. Overview

The emergence of the development of bio-based materials has extensively stimulated considerable interest in investigating their physical and mechanical properties toward relevant applications such as infrastructure [1], automotive [2] as well as electronic device [3,4]. To date, many studies have researched the numerous types of bio-based materials such as cellulose [5–9], lignin [10], chitin-chitosan [11–14], polylactic acid [15,16] and soy-protein isolate [17] in order to meet possible requirements in engineering applications. This was probably due to the reason that bio-based materials have been confirmed theoretically and experimentally on environmental protection, non-toxic and value-added from agricultural product [18–21]. The concept of renewability and sustainability of bio-based product was strongly employed in order to use the resource with higher efficiency.

Cellulose, one of the bio-based materials, can be effectively derived either from a top-down approach, in which biomass was subjected to high shear forces in order to create smaller size of cellulose in suspension [22,23], or from a bottom-up approach, utilizing the biosynthesis of cellulose by bacteria [24], in which the most effective bacterial specie was *Acetobacter Xylinam*. The advantage of bacterial cellulose was related to the purity of the product. Cellulose prepared from bacteria was free from wax, lignin, pectin and hemicelluloses, which was commonly present in cellulose derived from plants. Moreover, cellulose prepared from bacteria could be effectively controlled on its repeating unit and the molecular weight on fermentation process. However, from the viewpoint of industrial commercialization, the cost of cellulose prepared from bacteria was relatively high. The use of bacterial cellulose-based material for sustainable energy was therefore limited if any mass production was to be continued.

For engineering properties, cellulose prepared from plant was preferred for mass production due to cost effectiveness. The concept of renewable and sustainable product for cellulose-based material was strongly considered. From the fundamental point of view, cellulose remarkably exhibited high stiffness, strength as well as high thermal stability. This was probably due to the fact that the structure of cellulose was considered as a network structure, leading to hold and support the applied external force if cellulose was developed for engineering research and industry community [25]. Moreover, the coefficient of thermal expansion is as low as 0.1 ppm/K [26]. Young's modulus of its single fibril was measured to be as high as 114 GPa [27]. It also has attractive features of high degree of crystallinity of 89% [28], high degree of polymerization (14,400) [29] and high specific surface area (37 m^2/g) [30]. Owing to the excellent physical and chemical properties of cellulose, it was extensively being pushed to develop from academic research to industrial commercialization. Functionalization of cellulose can effectively generate greater economic uses for cellulose rather than burning as an energy recovery source. The desirable properties of cellulose can generate cellulose-based composites having a wide array of application sectors.

To date, the objective of my research group is focused on the development of cellulose for use in sensors application and, if appreciable, any sensors prepared from cellulose for energy science and technology were one of our objectives. It was important to note that sensor is considered an important part of an energy power plant. Capacitive sensor is mandatorily required for energy storage device. Capacitive sensors can be employed to investigate the amount of electric charge that can be kept and subsequently used in relevant applications.

For electro-active materials, or strain sensors, they can be defined as a change in size or shape when stimulated by an applied electric field [31,32]. This made electro-active materials attractive for integration inside micro-electromechanical systems. In industrial commercialization, strain sensors can be used in many energy-based research areas such as micro-actuators [33,34], robotics [35] as well as vibration control applications [36–38].

For gas-based sensors, the amount of residual and production yield from the product of bio-based energy such as bio-ethanol can be determined using a gas sensor. Bio-based ethanol can be effectively prepared from residuals of biomass product. The odor from the fermentation process can be effectively predicted using a gas-based sensor. Moreover, in the process of fermentation, the experiment is commonly conducted at elevated temperatures. Temperature-based sensors may also be required.

On the other hand, energy can be produced from hydro-power plants. Water was commonly evaporated in the steam boiler and it was consequently used to monitor the system for power plant. Because the concept of steam boiler was involved in heating of water, a humidity sensor was employed. The use of humidity sensors can be controlled by the appropriate percent of relative humidity (RH), which is commonly related to temperature. Heat generation as well as electricity can be effectively produced for both quality and quantity due to the excellent humidity of the sensor.

UV sensor is also an important device for solar-based energy. It is important to note that solar-based energy, for example, dye synthesized solar cell (DSSC), can produce electricity by applying light on both sides of a DSSC electrode. Light can be interacted on both electrodes and photon can be separated; free ion is then stored. Owing to this concept, UV-based sensor is important to control the amount of UV that can effectively predict the quality of light as well as to design any solar-based material that has high efficiency in the energy production process.

To date, cellulose-based composites have been used as sensing materials, and have increasingly gained development, respectively [39–41]. Owing to some particular advantages, cellulose has high chemical, physical and thermal stability, which consequently allows its application under different operating conditions. The engineering properties of cellulose can be modified from a cheap process. The controllable properties of cellulose can be versatile depending on molecular weight, size as well as structure. Modification of cellulose can be therefore versatile for sensor-based energy materials.

In this review article, we wish to present the theoretical background of cellulose following the modification of cellulose properties and cellulose-based composite preparation. Lastly, the development of cellulose and its performance for sensors for energy science and technology are highlighted.

2. Cellulose and its derivatives

2.1. Cellulose derived from plant

Cellulose was remarkably considered to be the most abundant organic compound mainly derived from biomass. The primary occurrence of cellulose was the existing lignocellulosic material in forests, wherein wood is considered as the most important source. Other cellulose-containing material may tentatively include agricultural residues, water plants and grasses. However, from the viewpoint of industrial commercialization, cellulose, the most common biopolymer, has been used for centuries as a raw material from trees and other plants in various applications. The worldwide production of this biopolymer is estimated to be between 10^{10}–10^{11} t each year [42] and only about 6×10^9 t is processed by paper, textile, materials and chemical industries [43].

Cellulose was first isolated from plant matter by French chemist Anselme Payen in 1839 [44]. He reported that cellulose

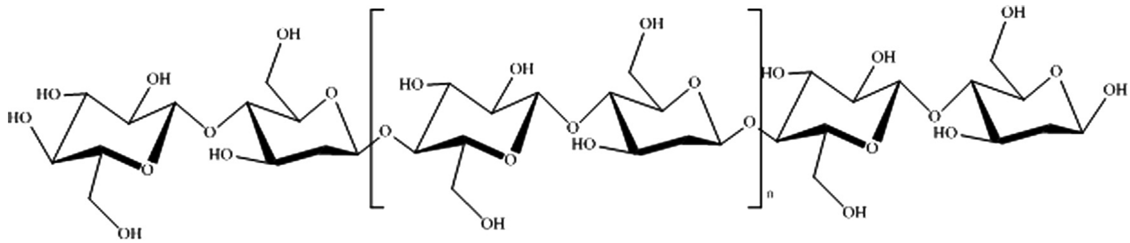

Fig. 1. Structure of cellulose.

has an identical structure as starch, but it exhibits a difference in structure and properties. The physical and chemical aspects of cellulose have been intensively studied. However, in wood structure, cellulose can be found in the cell wall of plants and the orientation of cellulose normally in vascular bundles was considered as a framework in order to support any applied external force [45]. Nowadays, its unique hierarchical structure no longer holds any secret. Utilization of cellulose in various applications requires a proper investigation of its physico-chemical characteristics in order to understand the chemical structure and physical behavior. For plants, the amount of cellulose and its extraction were varied depending on plant to plant, soy condition, environment as well as lifetime. Case-by-case study of cellulose extraction and its derivative should be individually employed. To date, cellulose is commonly known as a polysaccharide with the common formula $(C_6H_{10}O_5)_n$, and consisting of a linear chain of several hundreds to over thousands of linked glucose units. The degree of polymerization (DP) is approximately 10,000 for cellulose chains in nature and 15,000 for native cellulose cotton [42]. Fig. 1 exhibits the chemical structure of cellulose.

According to cellulose preparation, it is commonly known that cellulose can be produced from plants or bacteria. Cellulose can be successfully extracted from plants such as wood, flax, hemp, sisal or cotton. The amounts of cellulose and extraction process were varied from plant to plant, depending on soy condition as well as lifetime. For plants, cellulose is found in a composite form composed of polymers, lignin and hemicelluloses. They are physically and chemically bound together. Lignin is theoretically considered as adhesive, holding cellulose and hemicelluloses. Cellulose is considered as the main part of a plant structure, whereas hemicellulose, or sometimes called medium phase, acted as media in plant structures in order to connect both lignin and cellulose. In general, there was pectin in this plant structure, but the amount of pectin was too small compared to the other three compositions. In order to effectively purify cellulose from plants, the removal process of lignin, hemicelluloses and other impurities should be well controlled depending on plant to plant.

2.1.1. Mechanical treatment of cellulose suspension

2.1.1.1. Homogenizer and microfluidizer. Homogenizer is often used to manufacture microfibrillated cellulose. For use in homogenizer process, cellulose suspension was pumped at high pressure and consequently fed through a spring-loaded valve assembly. The process of open and close valve was very rapid, and fiber was therefore subjected to a large pressure drop under high shearing force. In the experiment, the applied pressure was very high and resulted in high shear rate and it subsequently provided a very thin cellulose particle. In the experiment, the chamber dimension was typically designed for 200–400 μm and external pressure was applied at 2000 bar [46]. The shear rate consequently reached up to $10^7\ s^{-1}$ and it resulted in the formation of very thin cellulose fibers [47]. The size of the chamber of the homogenizer process needs to be carefully controlled in order to obtain uniformity in size of the cellulose particle [48].

2.1.1.2. Grinding process. The grinding process used was called grinder. The principle consisted of the breakdown of the cell wall structure owing to the shearing forces generated by the grinding stone with a high speed of grinding rotation. The pulp was passed between a static grind stone and a rotating grind stone with about 1300 rpm [49]. Then, cellulose that composed the cell wall in a multilayer structure was therefore individualized from wood. The size of cellulose can be effectively controlled by grinding round and speed. As a longer round was spent, the size of cellulose was reduced to the nano-scale level. However, there is no significant change in morphological properties.

2.1.1.3. Cryocrushing. Cryocrushing is nowadays rarely used in cellulose suspension preparation. The first report on this cryocrushing process was in 1997 [50]. This process typically consisted of the crushing of frozen pulp with liquid nitrogen [51]. Ice crystals within the cells were then formed, and under mechanical crushing, they slashed the cellular wall and released the wall fragment. Typically, the size of cellulose was 20–40 nm and the length can be varied to several thousands of nanometers. It is commonly used to exact cellulose from agriculture crop and by-products such as flax and hemp.

2.1.2. Pre-treatments

Prior to using cellulose suspension with higher efficiency, many strategies have been put forward to modify cellulose on both product quality and process control. Pre-treatment of cellulose facilitated the disintegration of cellulose from wood fiber pulp, effectively resulting in increasing the swelling in water. The role of pre-treatment was strongly considered for cellulose modification due to less energy consumption. It is important to note that mechanical isolation process for cellulose gained high energy consumption [52].For the pre-treatment scenario, several approaches have been put forward to obtain fibers that were less stiff and cohesive and therefore consequently reduced the energy of the production process. To date, it is remarkable to note that there are three alternative methods; it was limited hydrogen bond or adding a repulsive charge, and decreasing the degree of polymerization or the amorphous link between individual cellulose particles.

2.1.2.1. Enzymatic pre-treatment. From the viewpoint of cellulose preparation process, enzyme was commonly used to modify cellulose and to degrade lignin, hemicelluloses and any other impurities while maintaining the cellulose portion [53]. It is very well-known that unmodified cellulose is composed of lignin, hemicelluloses, pectin, protein, ash, salt and mineral. To purify cellulose from any impurities, advanced application mandatorily needs to be performed. Moreover, the use of enzymes can significantly provide advantages in the restrictive hydrolysis of several elements or the selective hydrolysis of specified components in cellulose fibers. In a typical experiment, cellulose suspension contains many impurities. To purify cellulose, a set of

enzymes such as cellulases and endoglucanase is required to degrade any impurities [54].

2.1.2.2. TEMPO-mediated oxidation pre-treatment. The most effective and common method for pre-treatment is called "TEMPO mediated oxidation". This pre-treatment is the most promising method for effecting the surface modification of native cellulose. The carboxylate and aldehyde functional groups can be introduced into solid native cellulose under aqueous and mild conditions [55,56]. For the production process, it can be saved for energy consumption from the mechanical treatment process. In this pre-treatment, the basic principle is to oxidase cellulose. Consequently, the nanofibrils within the fibers separate from each other better due to the repulsive forces among ionized carboxylates, which overwhelm the hydrogen bond holding them together.

2.1.2.3. Carboxymethylation and acetylation. Carboxymethylation is one type of effective chemical treatment. The concept of this pre-treatment is to increase the anionic charges in the formation of carboxyl groups on the surface of the cellulose. As a result, this chemical treatment made the fibrils highly charged and easier to liberate into nano-scale sizes [57,58]. However, this technique requires high energy consumption for pre-treatment during passing through a microfluidizer. Moreover, it can be found that very high concentrations of salt or too low pH could cause a rapid agglomeration of the fibers. On the other hand, due to this reason, acetylation pre-treatment was performed. The grafting of acetyl moieties aimed to decrease the hydrophilic properties and to enhance the chemical affinity between cellulose and non-polar solvents [59,60]. Furthermore, carboxymethylation was further developed if cellulose based polymer composite was performed. The grafted acetyl groups reduced the hydrogen bonding between cellulose and therefore allow for superiority on dispersibility in an apolar polymer matrix.

2.1.3. Post-treatment

Post-treatment is theoretically considered as the last step prior to using cellulose with the desired properties and performance. Compared to pre-treatment and mechanical process, the use of post-treatment is still small. Numerous approaches have been extensively considered on the use of pre-treatment in order to reduce the energy consumption during the cellulose production process. It is commonly known that post-treatment is required from the novel prospective of application.

From the prospective of application, post-treatment is quite specific to consider. Recently, the development of barrier properties against moisture and gas permeation has been extensively considered. The modification of cellulose surface by solvent-exchange and epitaxial thin film growth was employed [61–63]. Si-O barrier film was deposited by means of plasma-enhanced chemical vapor deposition (PECVD) technique on the surface of bacterial cellulose nanocomposite in order to reduce the water absorption ability. Also, acetic anhydride was added to cellulose suspension in toluene after the solvent exchange process for having a hydrophobic feature [64]. Post-treatment was sometimes considered on chemical modification. Acetylation reaction was employed with bacterial cellulose-based nanocomposite films in order to improve the optical properties [65] and thermal degradation resistance [66]. However, the silylation process by using of chlorodimethyl isopropylsilane was also commonly employed to modify the surface for use as a hydrophobic feature [67,68]. Generally, the most powerful concept for post-treatment was strongly attempted for hydrophobic feature of surface properties. Owing to the nature of cellulose, it is commonly known that the hydroxyl group was facile to absorption water and it consequently decreased the performance of cellulose if it was fabricated for any applications.

Currently, post-treatment is strongly considered by the grafting of coupling agents and metal particles at the hydroxyl position of the cellulose. Grafting process strongly induced the surface functionality of cellulose if it was fabricated as a composite structure. In recent years, research has strongly attempted to graft carbon nanotubes at the hydroxyl position of the cellulose for dielectric and piezoelectric responses, which was considered to result in the electro-mechanical characteristic of cellulose [69–71]. This concept of carbon nanotube can be used as strain and gas sensor.

Numerous treatments on cellulose and cellulose-based composites have been developed. The primary objective was to consider the energy consumption of cellulose production so as to comply with a sustainable political agenda and garner market interest. Another target was to improve cellulose product and production process in order to produce novel bio-based materials that can be widely employed in many types of active sensor.

3. Cellulose-based composite

3.1. Cellulose derived from plant-based composite

Cellulose-based composite was theoretically defined as two phase materials (one was cellulose and the other was commonly considered a polymer). Cellulose-based composites not only provided significant efforts in terms of biodegradability and favorable CO_2 balance growth with the awareness of consumers for sustainability in the use of materials but also offered a value-added concept on agricultural product and waste. Cellulose-based composites have been extensively researched. It is well-known that cellulose has emerged in industrial commercialization in composites as a reinforcement with both petrochemical-based polymer and bio-based polymer matrices. An example of cellulose-based polymer matrix composite and its comprehensive potential application in research has been discussed.

3.1.1. Polylactic acid (PLA)-based cellulose composite

In the framework of environmentally friendly processes and products, polylactic acid is considered as the most effective biopolymer for bio-based composites, owing to the concept of renewability, biodegradability and biocompatibility. From the viewpoint of preparation route, polylactic acid is a biodegradable thermoplastic polyester manufactured by biotechnological processes from renewable resources. Corn, the common source of biomasses, is the most effective source for providing high-purity polylactic acid. The design of polylactic acid-based composite is strongly encouraged to develop a green scenario [72]. In recent years, the production of polylactic acid has formally announced a production capacity of 140,000 t/year for the commodity market [73,74]. It can be consequently considered that polylactic acid gained more and more interest as a valuable bio-resource for any alternative application.

From the viewpoint of polylactic acid research community, it is very well-known that polylactic acid exhibited low molecular weight and relatively low thermal resistance. In addition, the polylactic acid synthetic route commonly requires high temperature in the polycondensation process, continuous water removal and long reaction time. This consequently reduced the efficiency of polylactic acid in industrial commercialization. Relevant engineering properties of polylactic acid can be significantly improved by modifying the polylactic acid-based composite form. Reinforcement with cellulose is strongly encouraged. The properties of cellulose are evident in terms of mechanical and thermal resistance including high stiffness, low density, unique morphology,

high aspect ratio as well as high melting temperature. The incorporation of cellulose into polylactic acid can adjust the engineering properties of polylactic acid, and the open-wide vision of the use of polylactic acid can be extensively addressed.

3.1.2. Poly-hydroxy butyrate (PHB)-based cellulose composite

PHB has received much attention on bio-based research in recent years with a large number of publications ranging in topic from biosynthesis, microstructure, thermal and mechanical properties as well as biodegradation. Numerous research works have been driven by the availability of PHB from renewable resources and the similarity of PHB-relevant properties to those of conventional plastics.

The design of PHB and cellulose composite has been evident to date. Barkoula et al. studied the effects of cellulose fiber and hydroxyvalerate contents as binary blend composite [75]. The amount of raw materials, biodegradability and the influence of manufacturing condition on the engineering properties of composite were evaluated. It is important to note that this composite exhibited low impact strength if injection molding is used for fabrication. The tensile strength significantly decreased in the initial stage of degradation. Hence, many approaches have been developed on the interface of PHB-based cellulose composite. Interfacial properties improvement can be enhanced by the addition of 4,40-thiodiphenol at various concentrations. This additive can effectively form a hydrogen bond with many functional groups at the surface of the cellulose, leading to more adherent features of cellulose in the PHB composite [76]. On the other hand, prior to composite preparation between cellulose and PHB, chemically modified fiber by PEG grafting on cellulose was investigated. Better adhesion can be subsequently observed if this chemically modified cellulose is fabricated with PHB by compression molding [77]. More and more research on PHB can be extensively developed and applied in many forms of cellulose [78–80]. Engineering properties including mechanical, thermal and thermo-mechanical properties are consequently evaluated.

3.1.3. Starch-based cellulose composite

Starch as an agro-sourced polymer has received much attention in bio-based composites recently due to its strong advantages such as low cost, wide availability and total compost-ability without toxic residues. However, despite considerable commercial product being available, the engineering properties of starch-based composite have to be enhanced to enable such materials to be truly competitive with petroleum-based plastic over a wider range of applications.

Although starch-based composites provided significant interest in terms of cost effectiveness, the use of starch-based composite is limited in engineering application due to poor process-ability, low mechanical properties and poor long-term stability. In the glassy state, starch tends to be brittle and is very sensitive to moisture. In order to fabricate starch, it is often converted into a thermoplastic starch. It is obtained after disruption and plasticization of native starch by applying thermo-mechanical energy in a continuous extrusion process. Therefore, numerous efforts on formulation development of starch have been developed on both thermal and rheological properties [81–87]. From the viewpoint of cellulose production process, starch has been used to fabricate with cellulose as a composite feature. It is seen that numerous forms of cellulose can be successfully fabricated with starch such as flax [88], hemp [89], ramie [90] and cassava bagasse [91]. The advantage of starch-based composite for cellulose is extremely focused on truly green composite features. The compostable and biodegradable concept can be successfully developed without toxic residual. However, thermal stability, moisture resistance and oxygen barrier properties still need to be developed for excellent engineering performance.

3.1.4. Polyurethane (PU)-based cellulose composite

Recent progress in polyurethane-based composite has been extensively reviewed [92]. From the past, it has increasingly been used in a variety of applications due to comfort, cost benefits, energy saving and potential environmental soundness. The various types of polyurethane products were generally prepared in the form of flakes, powders and pellets. In the industry, it is found that the application of polyurethane and polyurethane-based composite is versatile. It can be prepared as foam-like structure for automotive interior [93,94], foot wear [95] and medical device [96,97]. From a structural point of view, polyurethane exhibited excellent mechanical properties, high thermal resistance and high chemical resistance. The role of polyurethane was subsequently employed in many engineering sectors. For the cellulose composite community, polyurethane was developed as many ways of composite. It reduced water absorption ability to cellulose and provided high flexibility. In 2012, Ummartyotin et al. reported the use of polyurethane as a matrix for the reinforcement of cellulose composites. The use of this matrix can lead to enhancement of the mechanical properties and to reducing the water absorption on cellulose. This composite exhibited remarkable application as an effective organic light emitting diode (OLED) substrate with additional features of flexibility and transparency [3]. On the other hand, it can be found that the polyurethane can be effectively used in membrane separation technology. Cellulose-based polyurethane can increase the stability in any pH media. Permeability of any active ions of the membrane can be controlled for being as long life-time for separation technology [98,99].

4. The challenges of cellulose-based composite for sensor materials

Sensor, one type of electronic device, is theoretically defined as a transducer that converts one form of energy into other amenable forms for further processing. Many types of sensors including gas sensor, chemical sensor, capacitive sensor, UV sensor and strain sensor have been well established in both academic and industrial research for energy science and technology. From the viewpoint of sensor materials, there was a prerequisite requirement on simple, sensitive and stable features suited for trace detection in a wide spectrum of applications ranging from lab-on-a-chip and in vivo biosensor to environmental monitoring and warfare agent detection, as opposed to the often employed sensitive, bulky and complicated instrumental methods. It is commonly known that in order to use sensors with higher efficiency, it must be compact, have a high speed for receiving and distribution for signal, be immune to environmental variation as well as able to resolve position down to the atomic scale. Fig. 2 shows the structure of a sensor. It is composed of receptor and transducer. Receptors are used to detect any active materials such as volatile gas, humidity and UV, while transducers are used to change any active materials to electric signal in order to be facile for engineering.

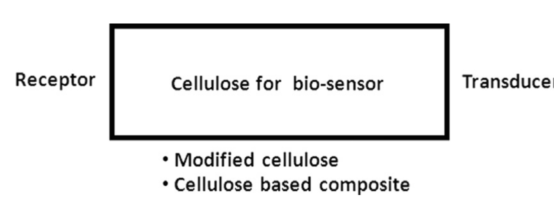

Fig. 2. Structure of sensors.

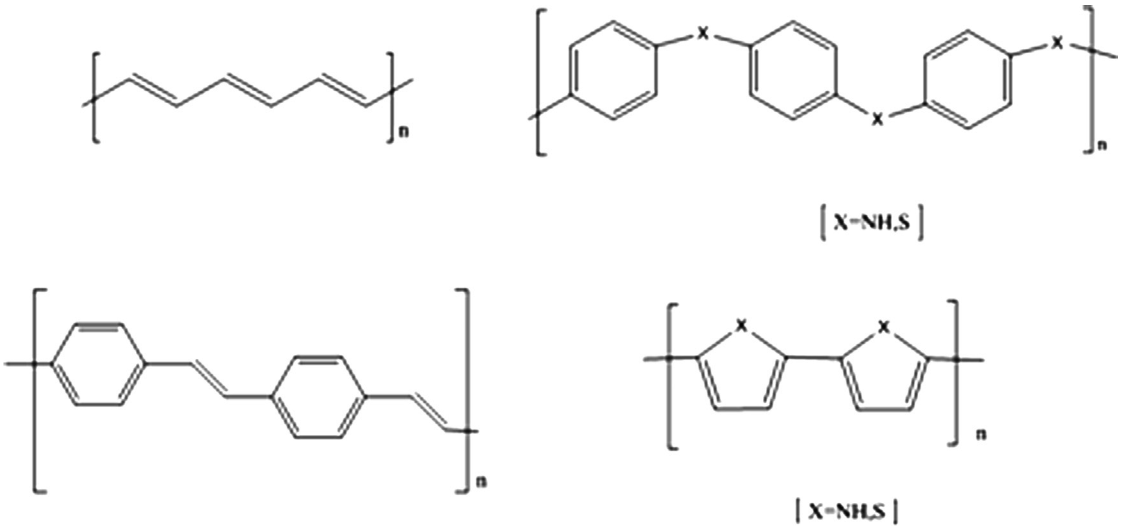

Fig. 3. Example of conductive polymer for gas-sensing applications; polyacetylene, polyphenylene, polypyrrole (X=NH), polythiophene (X=S), polyaniline (X=NH/N) and polyphenylene sulfide (X=S).

In order to evaluate the performance of a sensor, it is necessary to restrict the definitions for the characteristic of interest such as accuracy, precision, nonlinearity and resolution, which commonly defined as loosely and often vary between manufacturer and researcher [100]. Sometimes, the lack of universal standard makes it difficult to predict the performance of a sensor in some particular specifications or applications. From a fundamental point of view, many researchers have extensively conducted the feasibility of materials for use as sensors. The use of carbon-based materials [101,102], conductive polymers [103] and any form of active nano-scale material [104,105] has been researched.

For cellulose-based composite community, cellulose has been applied in many activities of sensor materials. It is important to note that cellulose can be effectively prepared as hydrogel [106] and composite form [107]. The structure of cellulose can be further designed to be sensitive in nano-scale structured materials [108], leading to several versatile applications of the sensor. Therefore, it has been highly stresses to develop for both academic research and industrial commercialization. With the framework of sensor materials prepared from cellulose, the fundamentals of sensor and the role of cellulose-based composite or any form of cellulose were discussed.

4.1. Gas detection sensor

Gas detection sensor has been extensively discussed regarding its structure, properties and relevant applications for many years. It is important to note that gas-sensing materials have been developed for environmental protection concern. From the structural point of view, it can be theoretically defined that gas detection sensor can be fabricated from two different sources of materials. One is focused on inorganic semiconductor metal oxides such as SnO_2 [109,110], TiO_2 [111–113], ZnO [114–116], WO_3 [117–119] or Fe_2O_3 [120–123]. The properties and performances of this material are generally enhanced by inserting a small amount of metal atom, called "doping process" [124–126]. The other one is focused on organic conducting polymer [127–130] such as polythiophene (PPT) [131–133], polypyrrole (PPy) [134–136] and polyaniline (PANI) [137–139]. Inorganic semiconductor metal oxide is unstable due to the ionic conducting charge on the surface, while organic conducting polymer has a free electron on its double bond along the polymer main chain. Moreover, the use of both materials is limited. It is notable that the use of inorganic semiconductor metal oxide requires high working temperature, therefore resulting in high energy or power consumption and latent safety concern. However, organic conducting polymer has received considerable interest as an effective material for ambient temperatures. However, it still had its own shortcomings such as low thermal stability, low response and very long response time, which can subsequently hinder potential application in the future. Numerous efforts have been extensively conducted on the research of combination between inorganic semiconductor and conductive polymer [140–142]. This combination can effectively offer not only significant enhancement of sensor ability, but also flexibility of materials if it is further applied in engineering applications. Fig. 3 shows the example of conductive polymer for a cellulose-conductive polymer binary blend system.

From the viewpoint of gas sensor, cellulose can be satisfactory in many aspects. It is important to note that not only cellulose-based composite with a conductive polymer can be used in gas sensor application but also cellulose itself can be chemically modified in structure to be used as a gas sensor. In case of cellulose base composite with conductive polymer or any inorganic particle, the use of cellulose-based composite can be versatile. The application of only inorganic particle is still limited in some applications if this displacement is required. Cellulose can therefore hold inorganic particles in order to gain higher flexibility and it is suitable for use as a portable form of gas sensor. For energy production such as bio-ethanol plant, the role of a portable gas sensor is very convenient to verify any active gas in the system.

Moreover, based on the chemical structure of cellulose, it contains three groups of hydroxyl group (OH-group). This functional group is highly active in order to chemically modify the OH-group. In the industry, multiwall carbon nanotube (MWCNT) particle chemically interacts with oxygen atom of cellulose and subsequently forms a network in between the cellulose fiber chain. Chemically modified MWCNT on the hydroxyl position of the cellulose can form a cellulose network and it can be used as ammonia gas sensing and chemical vapor sensor [143], respectively.

4.2. Humidity sensor

Humidity sensor, one type of frequently used sensor, has been extensively utilized in many research academic and industrial

areas. It is important to note that humidity sensor is widely used for industrial protection, environmental monitoring and protection, storage as well as human contact [144,145]. This is similar to a gas detection sensor; the high performance of a humidity sensor is also required to have linear response, rapid response time as well as chemical and physical stability. From the past, it is commonly known that inorganic materials or ceramic successfully develops and improves the engineering properties of a humidity sensor. Oxide spinel ceramic powder was successfully synthesized for use in a humidity sensor [146–152]. It can be found that the synthetic product was varied from bulk material to nano-scale level. The use of ceramic for humidity can be versatile, depending on the purity of the product. Although the use of ceramic materials for humidity provided high efficiency in terms of energy conversion, the brittleness of ceramic was still an issue if small displacement was required. Numerous efforts have been initially carried out for designing ceramic and polymer composites for a humidity sensor. Ceramic particle or any sensing particle was incorporated into the conductive polymer matrix [153–157]. It was found that the range scale of composite materials can be divided as bulk to nano-scale size. A conductive polymer can offer not only sensing ability but also increased flexible characteristic. This desired composite can be optimized on both sensing ability and mechanical properties.

From the viewpoint of bio-based composite, cellulose was generally fabricated as the host-matrix for ceramic particle encapsulation. The use of cellulose commonly provides high flexibility if the composite is applied under high load or high frequency of distribution. The other modification of cellulose-based composite is to blend with an organic conducting polymer. The cross-linked characteristic of organic conducting polymer and cellulose enhanced not only the mechanical properties, but also the sensing ability of this blend material. Moreover, it was found that the use of humidity sensor was varied with temperature. Cellulose can effectively provide high thermal and heat resistance [158]. The use of cellulose-based humidity sensor is encouraged if relevant application concerns elevated temperature dependence.

Moreover, the role of cellulose is not limited only to the chemical modification for a strain sensor. In 2011, Mahadeva et al. [158] investigated the feasibility of cellulose and polypyrrole nanocomposite for flexible humidity and temperature sensor. The feature of the materials was considered as smart-paper. Polypyrrole and cellulose-based composites were successfully obtained from in-situ polymerization technique. Cellulose was considered as matrix while polypyrrole was considered as particle reinforcement.

4.3. Ultraviolet sensor

UV sensor is widely used in many engineering sectors including environmental monitoring, military, medicine and wireless or space communication [159,160]. For bio-based composite for UV sensor, cellulose was considered as matrix and reinforced with organic conductive polymer, similar to gas detection and humidity sensor. Recently, in 2014, Jing et al. [161] presented a novel type of hybrid composite between inorganic and organic films based on polyoxometalates and cellulose. In this composite structure, cellulose and polyoxometalates can act as the matrix and particle reinforcement, respectively. The application of this UV sensor is involved in the production of visible-light photochromism properties. Compared to the other types of sensor, the role of cellulose in a UV sensor is still limited. Common feature is related to cellulose-based composites. Cellulose is considered as a matrix and the other reinforcements including conductive polymer and inorganic particle can be versatile, depending on the desired UV sensor performance. The main challenges of this sensor are based on organic conducting polymers, which are typically used as tunable materials for UV-sensitive devices. It was commonly used as light-sensing materials such as PEDOT: PSS, ZnO and ITO composite for use in light activation of UV [162–164]. UV absorption of organic materials can be easily tuned by tailoring the chemical structure; UV sensors based on organic materials generally seem to demonstrate more flexibility in realizing spectral selective response.

4.4. Strain sensor

Strain sensor, one type of effective electronic sensor, is commonly referred to as sensor and actuator or as an electro-mechanic sensor. The application of this sensor is very wide-ranging in the industry. For example, building, bridge, and other critical infrastructures are sometimes subjected to severe natural disasters, such as hurricanes, Tsunami and earthquakes. In order to prevent any catastrophic failure, it is effectively necessary to monitor the state of these infrastructures in real time using a strain sensor [165–167]. From the fundamental point of view, due to the wide use in outdoor applications, strain sensor with ultrahigh flexibility and stretch-ability plays a significantly key role in personal health monitoring, human-benign device as well as in highly sensitive devices, or sometimes called smart devices [168]. From the viewpoint of structure, this type of sensor is commonly fabricated as a thin film form. This film is preferably fabricated as ultra-thin, which gives it a higher efficiency. Strain sensor, sometimes called electro-mechanic sensor, theoretically uses nanoparticles with strong polarization in order to be used as active media for providing electric charge under applied external electric field. For cellulose composite, cellulose is generally used as a matrix for holding nanoparticles. This consequently provides strong polarization if an external electric field is applied. Moreover, cellulose is composed of three groups of hydroxyl (OH). The insertion of nanoparticles can be both chemically modified and physically incorporated. Recently, for example, O-Rak et al. successfully modified the structure of cellulose using multiwalled carbon nanotubes [69]. It was successfully integrated by covalent grafting on the hydroxyl of cellulose. Stronger polarization can be observed and subsequently exhibit the prerequisite properties on electro-active materials if the strain sensor is further developed. In addition, in 2008, Yun et al. [169] also found that cellulose can be prepared as a solution using the cotton pulp in LiCl/N,N-dimethylacetamide and then multiwalled carbon nanotube (MWCNT) can be grafted in the hydroxyl position in order to tailor the electro-mechanical properties. Fig. 4 exhibits the chemical modification of cellulose by covalently grafting with multiwalled carbon nanotubes at the hydroxyl position.

Another approach on the chemical modification of cellulose was studied for electro-mechanical properties or piezoelectricity. Kim et al. [170] investigated the orientation of cellulose in electroactive paper and it was found that 45 degree of angle is the optimized orientation angle that offers the most effective electro-mechanical properties. This property is important for strain sensors.

4.5. Capacitive sensor

Capacitive sensor is quite specific in electronic application research area. The development of this sensor is quite far beyond reality for bio-based materials. The prerequisite engineering properties of this sensor mandatorily require short-range nano-positioning applications. It is relatively low cost and can effectively provide excellent linearity, resolution and bandwidth. In order to use capacitive sensors with higher efficiency, modification of the surface of this material is required. This is probably due to the calculation of the dielectric properties, which are very dependent on frequency and temperature. In 2005, one experiment on

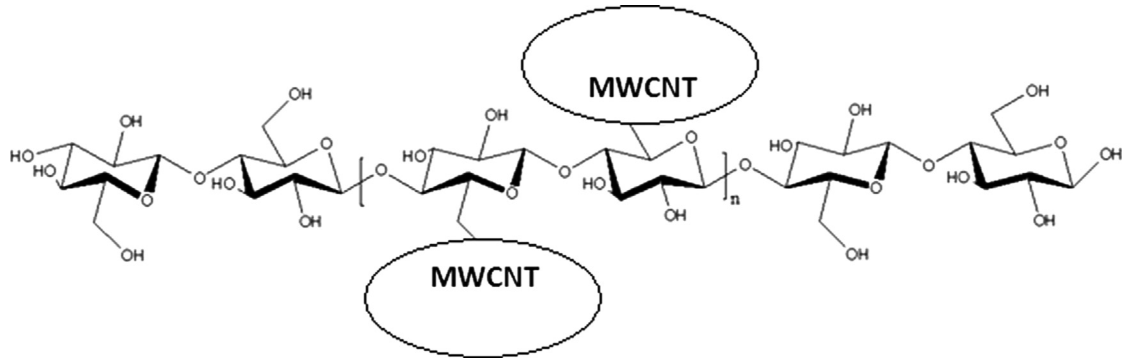

Fig. 4. Covalently grafted MWCNT at the hydroxyl position of cellulose.

capacitive sensor prepared from cellulose was successfully investigated [41]. Cellulose was chemically modified as cellulose acetate butylate (CAB) and it was further modified by cross-linking with melamine formaldehyde resin for use as capacitive materials. The experiment on sensor characteristics such as linearity, sensitivity, hysteresis, response time as well as maximum operating temperature was carried out.

Thus far, we wish to provide an overview on the development of cellulose on being used as sensor materials for energy science and technology. The development of cellulose from sustainable and renewable resource was extensively beneficial. Cellulose was described from fundamental theory to an approach as a sensor for energy science and technology. It was found that as a sensor, the penetration of cellulose era is still being developed. More and more strong improvement on the engineering properties is required in order to use cellulose with a higher efficiency in the sensor community.

5. Conclusion and outlook

In conclusion, a review describing cellulose and the physical and chemical modification has been presented. During the past three decades, cellulose and cellulose-based composites increasingly improved and developed in many areas of application. In this review, the application of cellulose for sensor was presented. Many forms of sensor including gas sensor, capacitive sensor, UV sensor, humidity sensor as well as strain sensor were discussed on the overview and the role of cellulose was presented. From the viewpoint of sustainable and renewable material, it was very encouraging to be value-added of cellulose for any possible application. Many approaches on sensor for energy science and technology have been discussed.

However, to date, the engineering properties and sensors' performance are still being developed. In order to satisfy the criterion of using cellulose for sensors with higher efficiency, more and more development on the engineering properties of cellulose is required in order to expand the use of cellulose as a sensor for energy science and technology.

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